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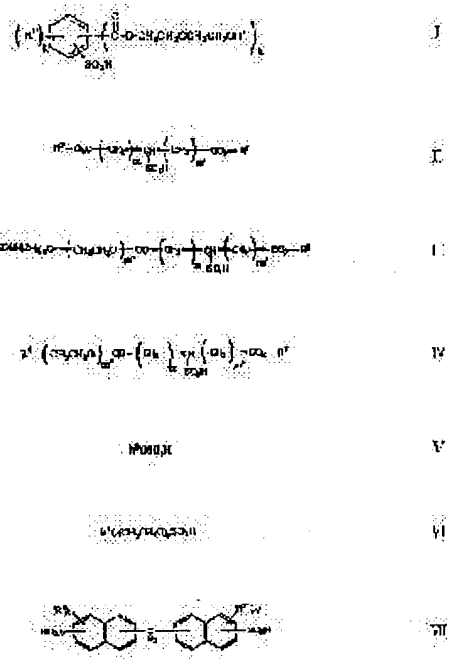
(54) ANTISTATIC AGENT USING CONDUCTIVE ORGANIC POLYMER COMPOSITION

(57)Abstract:

PURPOSE: To obtain a conductive compsn. which can form an antistatic film almost independent of moisture and excellent in water resistance and transparency by dissolving or dispersing, in a solvent, polyaniline or its deriv. and a specific protonic acid dopant in the doped state.

CONSTITUTION: This antistatic agent is a conductive org. polymer compsn. which comprises polyaniline or its deriv. and a dopant satisfying the relation: (mol.wt. of dopant)/N=350-2,000 (wherein N is the number of protonic acid groups having acid dissociation constants pKa of 4.0 or lower in one molecule), has a conductivity of 10-9S/cm or higher, and is a dispersion or a soln. in the doped state. Pref. examples of the dopant are compds. represented by formulas I to VII (wherein R1 to R4, R7, R1' to R4', and R7' are each H, etc.; R5 is a 20-40C alkyl, etc.; R6 is a 5-20C alkyl, etc.; R is 1-5; K' is 0-4; K+K' is 5; m, m', and m" are each 0-5; (p) is 1-5; and q and q' are each 1-6).



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[Date of request for examination] 28.09.2001

[Date of sending the examiner's decision of rejection]

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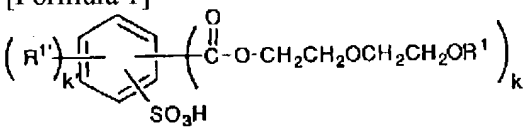
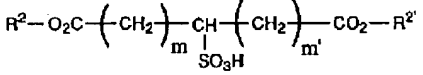
CLAIMS

[Claim(s)]
[Claim 1] The antistatic agent using the conductive organic polymer constituent with which it consists of a poly aniline and/or its derivative (A), and (molecular weight of a dopant) a proton acid dopant (B) of /N=350-2000 (the acid dissociation constant electric dissociation exponent in N=1 molecule is the number of 4.0 or less proton acid radicals), and conductivity is characterized by distributing or dissolving in a dope condition above 10-9 (S/cm).
[Claim 2] The antistatic agent using the conductive organic polymer constituent according to claim 1 by which a dopant is expressed with a formula (1).
[Formula 1]



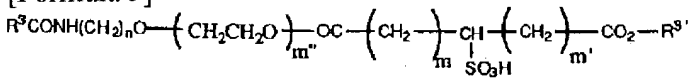
式 (1)

(Among the formula, when hydrogen or a carbon number shows the alkyl group of 1 to 15, an alkenyl radical, an alkylthio alkyl group, an aryl group, an alkyl aryl radical, an arylated alkyl radical, an alkoxyalkyl group, and an aryloxy alkyl group and exists, R1 may be the same and may differ.) [two or more] R1' shows hydrogen, an alkyl group, an alkenyl radical, an alkoxy group, an alkylthio group, an alkylthio alkyl group, an aryl group, an alkyl aryl radical, an arylated alkyl radical, an alkyl sulfinyl group, an alkoxyalkyl group, an aryloxy alkyl group, an alkyl sulfonyl group, an alkoxy carbonyl group, a carboxyl group, a nitrile group, a hydroxy group, a nitro group, or a halogen, and when more than one exist, even if the same, they may differ. k shows the integer of 1 to 5, k' shows the integer of 0 to 4, and it is k+k' =5.
[Claim 3] The antistatic agent using the conductive organic polymer constituent according to claim 1 by which a dopant is expressed with a formula (2).
[Formula 2]



式 (2)

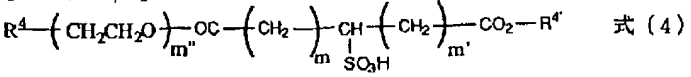
the inside of a formula, R2, and R2' are the same -- or you may differ and hydrogen or a carbon number shows the alkyl group of 5 to 15, an alkenyl radical, an alkylthio alkyl group, an aryl group, an alkyl aryl radical, an arylated alkyl radical, an alkoxyalkyl group, and an aryloxy alkyl group. m and m' shows the integer of 0 to 5.
[Claim 4] The antistatic agent using the conductive organic polymer constituent according to claim 1 by which a dopant is expressed with a formula (3).
[Formula 3]



式 (3)

the inside R3 of a formula and R3' are the same -- or you may differ and hydrogen or a carbon number shows the alkyl group of 5 to 20, an alkenyl radical, an alkylthio alkyl group, an aryl group, an alkyl aryl radical, an arylated alkyl radical, an alkoxyalkyl group, and an aryloxy alkyl group. m, m', and m" show the integer of 0 to 5. n shows the integer of 1 to 5.
[Claim 5] The antistatic agent using the conductive organic polymer constituent according to claim 1 by which a dopant is expressed with a formula (4).

[Formula 4]



式（4）

(As for the inside R4 of a formula, hydrogen or a carbon number shows the alkyl group of 5 to 20, an alkenyl radical, an alkoxy group, an alkylthio group, an alkylthio alkyl group, an aryl group, an alkyl aryl radical, an arylated alkyl radical, an alkyl sulfinyl group, an alkoxyalkyl group, and an aryloxy alkyl group, and, as for R4', hydrogen or a carbon number shows the alkyl group of 5 to 20, an alkenyl radical, an alkylthio alkyl group, an aryl group, an alkyl aryl radical, an arylated alkyl radical, an alkoxyalkyl group, and an aryloxy alkyl group.) m, m', and m" show the integer of 0 to 5.

[Claim 6] The antistatic agent using the conductive organic polymer constituent according to claim 1 by which a dopant is expressed with a formula (5).

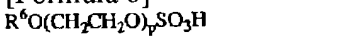
[Formula 5]

式（5）

(As for the inside R5 of a formula, a carbon number shows the alkyl group of 20 to 40, an alkenyl radical, an alkylthio alkyl group, an aryl group, an alkyl aryl radical, an arylated alkyl radical, an alkoxyalkyl group, and an aryloxy alkyl group.)

[Claim 7] The antistatic agent using the conductive organic polymer constituent according to claim 1 by which a dopant is expressed with a formula (6).

[Formula 6]

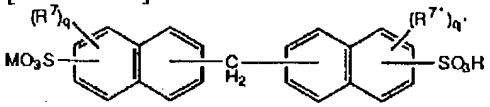


式（6）

(As for the inside R6 of a formula, a carbon number shows the alkyl group of 5 to 20, an alkenyl radical, an alkylthio alkyl group, an aryl group, an alkyl aryl radical, an arylated alkyl radical, an alkoxyalkyl group, and an aryloxy alkyl group, and p shows the integer of 1 to 5.)

[Claim 8] The antistatic agent using the conductive organic polymer constituent according to claim 1 by which a dopant is expressed with a formula (7).

[Formula 7]



式（7）

(M shows the cation (except for a proton) of monovalence, such as sodium ion, potassium ion, and ammonium ion, among a formula.) When hydrogen, an alkyl group, an alkenyl radical, an alkoxy group, an alkylthio group, an alkylthio alkyl group, an aryl group, an alkyl aryl radical, an arylated alkyl radical, an alkyl sulfinyl group, an alkoxyalkyl group, an aryloxy alkyl group, an alkyl sulfonyl group, an alkoxy carbonyl group, a carboxyl group, a nitrile group, a hydroxy group, a nitro group, or a halogen is shown and it exists [two or more], R7 and R7' may be the same, and may differ. q and q' shows the integer of 1 to 6.

[Claim 9] Claims 1-7 or the antistatic agent for resin fabrication articles using at least one sort of conductive organic polymer constituents given in eight.

[Claim 10] Claims 1-7 or the antistatic agent for plastic film using at least one sort of conductive organic polymers given in eight.

[Claim 11] Claims 1-7 or the antistatic agent for synthetic papers using at least one sort of conductive organic polymers given in eight.

[Claim 12] Claims 1-7 or the antistatic agent for fiber using at least one sort of conductive organic polymers given in eight.

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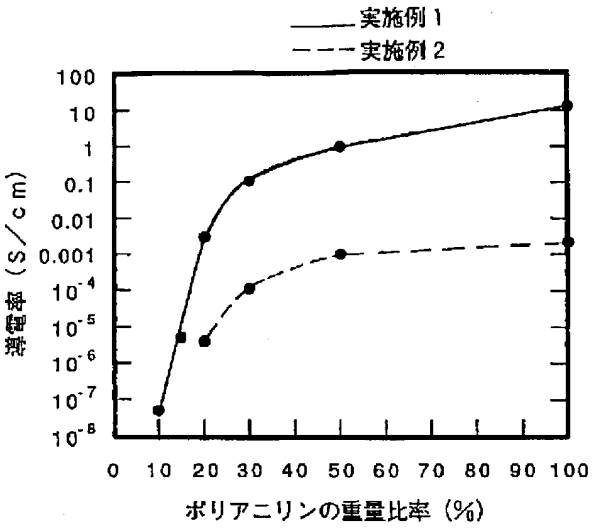
Drawing selection Representative drawing



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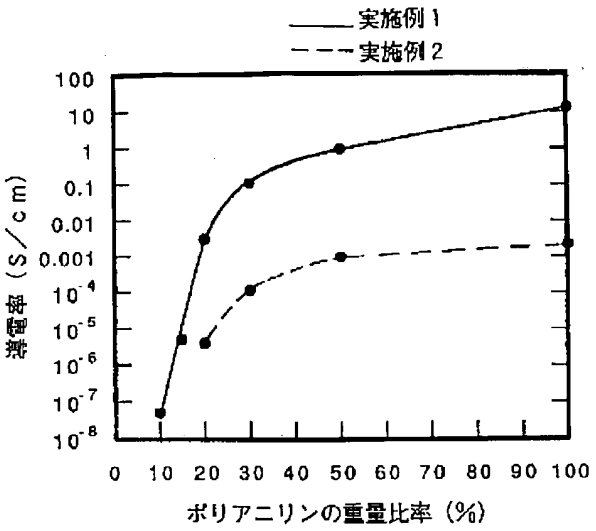
Drawing selection [Representative drawing]



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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates to the antistatic agent using the conductive organic polymer constituent containing the poly aniline which is distributing or dissolving in the general-purpose organic solvent and the aquosity solvent in the state of a dope (condition that a dopant lives together), and/or its derivative. Since it distributes or dissolves in a solvent in the state of a dope, the organic polymer constituent used for this invention can apply the solution or dispersion liquid of this constituent to a surface of metal directly, and can be dried. The obtained conductive thin film is useful to electrification prevention of a resin fabrication article, a film, a synthetic paper, fiber, etc.
[0002]
[Description of the Prior Art] Since it is electrified by high insulating materials, such as a resin fabrication article, plastic film, a synthetic paper, and fiber, and they often cause a serious failure by friction, exfoliation, etc., they need to carry out electric conduction processing of the front face for electrification prevention. As a conventional cure, it is i. ii which applies the surface active agent of ionicity There is adding conductive fillers (carbon black etc.) etc. However, in the antistatic agent of ionicity, it is i. Conductivity falls under low humidity. ii which runs short of antistatic ability It is surface electrical resistance 108 There is a fault, like an iii water resisting property with it difficult [to make it below (omega/**)] is low. To a conductive filler i) ii to which a base material black-izes and transparency worsens The reinforcement and the degree of hardness of a base material fall, and there is a fault -- original physical properties are spoiled. The antistatic agent which conquers these faults is called for. On the other hand, if plastic film, a synthetic paper, and the antistatic agent for fiber are developed using conductive organic polymers, such as the poly aniline, polypyrrole, and the poly thiophene, it is expected that the above-mentioned trouble is solvable. However, generally, the electrification nature organic polymer was non-**, and since it was insoluble to a general-purpose organic solvent and an aquosity solvent, was lacking in workability and had become the serious failure of application expansion.
[0003] Although the approach (JP,3-28229,A official report) which becomes processible was proposed about the poly aniline since the poly aniline of a dedope condition was meltable to a polar organic solvent of a certain kind, according to this approach, there was a trouble which needs the process which casts the poly aniline of a dedope condition and two processes of the process further doped with proton acid.
[0004] Although the proposal was made also about the approach (92 to WO22911 official report) of solubilizing the poly aniline of a dope condition, there were many troubles in using a strong corrosive solvent, it being harmful and using a superfluous corrosive proton acid dopant, etc. using the poly aniline industrially.
[0005] Although the method (JP,3-285983,A official report) of dissolving the poly aniline of a dope condition in the polar organic solvent which added ammonia or an volatile amine was also proposed, the trouble which the gas of harmful ammonia or an amine generates was in solvent removal and coincidence after molding.
[0006] Although the water-soluble poly aniline (JP,5-178989,A official report) of the self-doping mold which carried out direct coupling of the sulfonic group used as a dopant to the polymer frame was also proposed, the production process was complicated and the problem was in the cost side.
[0007] Although the approach (JP,2-69525,A official report) of carrying out the chemistry oxidation polymerization of an aniline or its derivative was proposed under existence of the purpose base material as an approach of making the coat of the poly aniline forming on a base material, to industrial large scale production, it was unsuitable.
[0008]

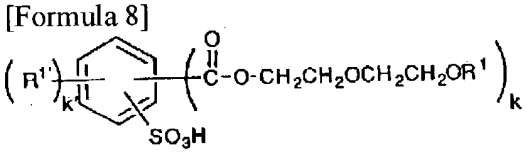
[Problem(s) to be Solved by the Invention] As a result of inquiring wholeheartedly that this invention persons should develop the cheap conductive poly aniline which may distribute or dissolve in a general-purpose organic solvent and an aquosity solvent in the state of a dope, the specific dopant found out that a solvent could be dissolved or distributed in the state of a dope, and it could deal in the poly aniline or its derivative. Moreover, the conductive thin film formed from the solution or dispersion liquid of the poly aniline constituent of this invention had few humidity dependencies, and found out that it was applicable to the antistatic film which was excellent in a water resisting property and transparency.

[0009]

[Means for Solving the Problem] Namely, this invention consists of a poly aniline and/or its derivative (A), and (molecular weight of a dopant) a proton acid toe punt (B) of /N=350-2000 (the acid dissociation constant electric dissociation exponent in N=1 molecule is the number of 4.0 or less proton acid radicals). It is a thing about the antistatic agent using the conductive organic polymer constituent with which conductivity is characterized by distributing or dissolving in a dope condition above 10-9 (S/cm). Moreover, it is the antistatic agent characterized by using the conductive organic polymer constituent with which the desirable dopant used in this conductive organic polymer constituent is chosen from the following formula (1) - a formula (7), and whose number is at least one. Furthermore, it is related with the resin fabrication article which this antistatic agent contained, plastic film, a synthetic paper, fiber, etc.

[0010]

[Formula 8]

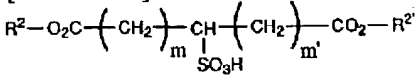


式 (1)

among the formula, 1 to 15, when the alkyl group of 2 to 12, an alkenyl radical, an alkylthio alkyl group, an aryl group, an alkyl aryl radical, an arylated alkyl radical, an alkoxyalkyl group, and an aryloxy alkyl group are shown preferably and more than one exist, even if R1 has hydrogen or a the same carbon number, it may differ. R1' shows hydrogen, an alkyl group, an alkenyl radical, an alkoxy group, an alkylthio group, an alkylthio alkyl group, an aryl group, an alkyl aryl radical, an arylated alkyl radical, an alkyl sulfinyl group, an alkoxyalkyl group, an aryloxy alkyl group, an alkyl sulfonyl group, an alkoxy carbonyl group, a carboxyl group, a nitrile group, a hydroxy group, a nitro group, or a halogen, and when more than one exist, even if the same, they may differ. As desirable R1', it is hydrogen, an alkyl group, an alkoxy group, an alkylthio group, an alkylthio alkyl group, an aryl group, an alkyl sulfinyl group, an alkoxyalkyl group, an alkoxy carbonyl group, a carboxyl group, a nitrile group, and a hydroxy group, and they are hydrogen, an alkoxy group, an alkylthio group, an alkylthio alkyl group, an alkyl sulfinyl group, an alkoxyalkyl group, an alkoxy carbonyl group, a carboxyl group, a nitrile group, and a hydroxy group still more preferably. k -- 1 to 5 -- desirable -- the integer of 2 to 4 -- being shown -- the integer of k'0 to 4 -- being shown -- k+k'=5.

[0011]

[Formula 9]

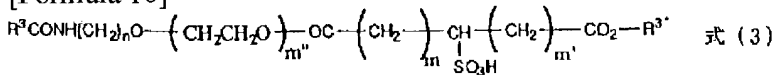


式 (2)

the inside of a formula, R2, and R2' are the same -- or you may differ and hydrogen or a carbon number shows the alkyl group of 5 to 15, an alkenyl radical, an alkylthio alkyl group, an aryl group, an alkyl aryl radical, an arylated alkyl radical, an alkoxyalkyl group, and an aryloxy alkyl group. As for desirable R2 and R2', a carbon number shows the alkyl group of 5 to 15, an alkylthio alkyl group, an alkoxyalkyl group, and an aryloxy alkyl group. m and m' shows the integer of 0 to 5. Preferably, m+m' is 1 to 8.

[0012]

[Formula 10]



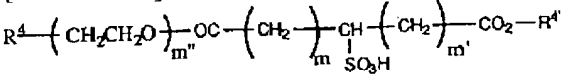
式 (3)

the inside R3 of a formula and R3' are the same -- or you may differ and hydrogen or a carbon number shows the alkyl group of 5 to 20, an alkenyl radical, an alkylthio alkyl group, an aryl group, an alkyl aryl radical, an

arylated alkyl radical, an alkoxyalkyl group, and an aryloxy alkyl group. Desirable R3 and R3' are the alkyl group of carbon numbers 7-20, an alkylthio alkyl group, an alkoxyalkyl group, and an aryloxy alkyl group. m, m', and m" show the integer of 0 to 5. Desirable m+m' is 1 to 8 and desirable m" is 2 to 5. n shows the integer of 1 to 5.

[0013]

[Formula 11]



式（4）

(As for the inside R4 of a formula, hydrogen or a carbon number shows the alkyl group of 5 to 20, an alkenyl radical, an alkoxy group, an alkylthio alkyl group, an aryl group, an alkyl aryl radical, an arylated alkyl radical, an alkoxyalkyl group, and an aryloxy alkyl group, and desirable R4 shows the alkyl group of carbon numbers 7-20, an alkoxy group, an alkylthio alkyl group, an alkoxyalkyl group, and an aryloxy alkyl group.) As for R4', hydrogen or a carbon number shows the alkyl group of 5 to 20, an alkenyl radical, an alkylthio alkyl group, an aryl group, an alkyl aryl radical, an arylated alkyl radical, an alkoxyalkyl group, and an aryloxy alkyl group, and desirable R4' shows the alkyl group of carbon numbers 7-20, an alkylthio alkyl group, an alkoxyalkyl group, and an aryloxy alkyl group. m, m', and m" show the integer of 0 to 5. Desirable m+m' is 1 to 8 and desirable m" is 2 to 5.

[0014]

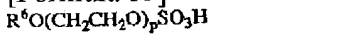
[Formula 12]

式（5）

(As for the inside R5 of a formula, a carbon number shows the alkyl group of 20 to 40, an alkenyl radical, an alkylthio alkyl group, an aryl group, an alkyl aryl radical, an arylated alkyl radical, an alkoxyalkyl group, and an aryloxy alkyl group.) Desirable R5 A carbon number shows the alkyl group of 20 to 40, an alkylthio alkyl group, an alkoxyalkyl group, and an aryloxy alkyl group.

[0015]

[Formula 13]

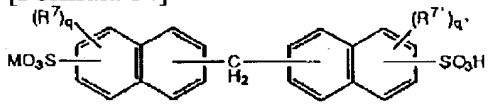


式（6）

(As for the inside R6 of a formula, a carbon number shows the alkyl group of 5 to 20, an alkenyl radical, an alkylthio alkyl group, an aryl group, an alkyl aryl radical, an arylated alkyl radical, an alkoxyalkyl group, and an aryloxy alkyl group, and, as for desirable R6, a carbon number shows the alkyl group of 7 to 20, an alkylthio alkyl group, an alkoxyalkyl group, and an aryloxy alkyl group.) p -- 1 to 5 -- the integer of 2 to 5 is shown preferably.

[0016]

[Formula 14]



式（7）

(M shows the cation (except for a proton) of monovalence, such as sodium ion, potassium ion, and ammonium ion, among a formula.) R7 and R7' show hydrogen, an alkyl group, an alkenyl radical, an alkoxy group, an alkylthio group, an alkylthio alkyl group, an aryl group, an alkyl aryl radical, an arylated alkyl radical, an alkyl sulfinyl group, an alkoxyalkyl group, an aryloxy alkyl group, an alkyl sulfonyl group, an alkoxy carbonyl group, a carboxyl group, a nitrile group, a hydroxy group, a nitro group, or a halogen, when it exists, may be the same, or may differ. [two or more] Desirable R7 and R7' show hydrogen, an alkyl group, an alkoxy group, an alkylthio group, an alkylthio alkyl group, an alkyl sulfinyl group, an alkoxyalkyl group, an aryloxy alkyl group, an alkyl sulfonyl group, an alkoxy carbonyl group, a carboxyl group, a nitrile group, a hydroxy group, a nitro group, or a halogen. q and q' shows the integer of 1 to 6.

[0017] In order to set in the dope condition and to distribute or dissolve the poly aniline, selection of a proton acid dopant is important. A suitable dopant needs to have a substructure with the high solvent compatibility which has a certain amount of spatial breadth besides a proton acid radical. The formula weight of poly aniline 1 unit in case protonation is carried out by the dopant is 181. In order to distribute or dissolve the soluble low

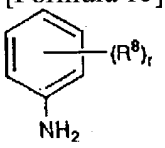
poly aniline principal chain by doping, it is surmised that the formula weight per 1 proton-acid radical of a dopant is [181 or more] required. this invention persons found out that the dopant which fills (the molecular weight of a dopant) / n=350-2000 (the acid dissociation constant electric dissociation exponent in N=1 molecule is the number of 4.0 or less proton acid radicals) was suitable, as a result of searching for various dopants along with this plan. The value 350 is about 2 twice [of the poly aniline] 181. Moreover, if this value becomes 2000 or more, the electronic conduction between the principal chains of the poly aniline will be barred for the steric hindrance by the dopant, and conductivity will fall. The proton acid radical on which an acid dissociation constant electric dissociation exponent exceeds 4 has the inadequate protonation to the poly aniline, and its conductivity of the constituent obtained is low.

[0018] It is 460-2000 still more preferably, and it is 520-2000 most preferably, and the values of ** (molecular weight of a dopant)/N are 400-2000 preferably, and the poly aniline of a dope condition becomes [it distributes, or is easy to dissolve and] a solvent at this order.

[0019] The proton acid compound shown by the above mentioned formula (1) - the formula (7) as an example of a suitable dopant is mentioned. These are all about 100 molecular weight number organic sulfonic acids. At the dopant shown by the formula (1) - the formula (6), it is RX. It is a polar low organic radical, and it is useful for mainly distributing or dissolving the poly aniline in a general-purpose organic solvent, and the dopant of a formula (7) is comparatively useful to having the sulfonate part of a hydrophilic radical and making it mainly distribute or dissolve in an aquosity solvent.

[0020] Although one kind or two kinds or more are sufficient as the aniline used at the time of an oxidation polymerization, or its derivative, it has the structure shown in the following formulas.

[Formula 15]



式 (8)

(The inside r of a formula is the integers from 0 to 5.) R8 each -- even when it is the same, you may differ and it is chosen from hydrogen, an alkyl group, an alkenyl radical, an alkoxy group, an alkanoyl radical, an alkylthio group, an aryloxy group, an alkylthio alkyl group, an aryl group, an alkyl aryl radical, an arylated alkyl radical, an alkyl sulfinyl group, an alkoxyalkyl group, an alkyl sulfonyl group, a carboxyl group, a halogen radical, a cyano group, a halo alkyl group, a nitro alkyl group, and a cyano alkyl group.

[0021] As an example, they are an aniline, ortho toluidine, meta toluidine, o-ethylaniline, m-ethylaniline, an o-ethoxy aniline, m-butyl aniline, m-hexyl aniline, m-octyl aniline, 2, 3-dimethylaniline, 2, 5-dimethylaniline, 2, 5-dimethoxy aniline, o-cyano aniline, 2, 5-SHIKURORO aniline, 2-BUROMO aniline, 5-chloro-2-methoxyaniline, 3-phenoxy aniline, etc.

[0022] As an oxidizer, a ammonium peroxydisulfate, a hydrogen peroxide, secondary salt-ized iron, etc. are used, and preferably, especially although a ammonium peroxydisulfate is used, it is not limited.

[0023] As an approach of obtaining the poly aniline used for this invention, the approach of adding the solution of an oxidizer and proton acid or the solution of an oxidizer is mentioned to the solution or suspension of an aniline or an aniline derivative, and proton acid. The polymerization conditions usually performed are applied to a polymerization. For example, within the limits of 48 hours, under ordinary pressure, reaction temperature makes a reaction mixture agitate and performs reaction time from 30 minutes between -10 degrees C and 40 degrees C. With [an acid dissociation constant electric dissociation exponent value] 4.0 [or less], the proton acid added at the time of an oxidation polymerization is not limited, and can mention polymer acids, such as polystyrene sulfonate, a polyvinyl sulfonic acid, and a polyvinyl sulphate, to organic-acid pans, such as inorganic acids, such as a hydrochloric acid, a sulfuric acid, a nitric acid, and perchloric acid, benzenesulfonic acid, p-toluenesulfonic acid, m-nitro benzoic acid, and a trichloroacetic acid.

[0024] Although the obtained poly aniline is dedoped and turns into a dedope poly aniline by processing by bases, such as aqueous ammonia, it can be again processed with desired proton acid, and can be made into a dope poly aniline. At the time of an oxidation polymerization, desired proton acid may be added and doped, and it adds to a dedope poly aniline, and is good also as a dope poly aniline.

[0025] 1Eq of a dopant is desirable to the poly aniline. Since a superfluous dopant has a possibility of carrying out induction of the corrosion, it is not desirable.

[0026] The organic solvent which the poly aniline constituent used for this invention may distribute or dissolve

can be especially used without a limit, if generally used as a general-purpose solvent. For example, polar solvents, such as halogenated hydrocarbon, such as aromatic hydrocarbon, such as carboxylic acids, such as ketones, such as nitril, such as alcohols, such as ether, such as a tetrahydrofuran and dioxane, a methanol, ethanol, isopropyl alcohol, and 2-n-butoxy ethanol, and an acetonitrile, and an acetone, a formic acid, an acetic acid, and a propionic acid, a xylene, and toluene, and chloroform, N-methyl pyrrolidone, dimethylformamide, and dimethyl sulfoxide, can be used. Furthermore, the aquosity solvent which the poly aniline constituent used for this invention may distribute or dissolve means a partially aromatic solvent with the organic solvent with which it mixes with water or water. Especially the ratio of water and an organic solvent is not limited. As the above-mentioned organic solvent, polar solvents, such as carboxylic acids, such as ketones, such as nitril, such as alcohols, such as ether, such as a tetrahydrofuran and dioxane, a methanol, ethanol, isopropyl alcohol, and 2-n-butoxy ethanol, and an acetonitrile, and an acetone, a formic acid, an acetic acid, and a propionic acid, N-methyl pyrrolidone, dimethylformamide, and dimethyl sulfoxide, can be used, for example. In the case of which, a corrosive and toxic low thing is desirable.

[0027] From the poly aniline constituent used for this invention, when fabricating a conductive thin film, it can mix with other matrix high molecular compounds. As such a matrix high molecular compound, polyester, polystyrene, polyethylene, a polyamide, polyimide, a polyvinyl chloride, polyvinyl acetate, polypropylene, an epoxy resin, phenol resin, silicone resin, a styrene-butadiene copolymer, polybutadiene, fluorine resin, a polysiloxane, a polycarbonate, a polyacrylonitrile, polymethylmethacrylate, ABS plastics, etc. are mentioned.

[0028] For example, when a high molecular compound is polyester, the side chain of a dopant is made to contain many ester bonds, or when a high molecular compound is a polyamide, compatibility [as opposed to the matrix high molecular compound of a dope condition poly aniline in making the side chain of a dopant contain many amide association etc.] can be raised. Moreover, the mixing ratio of a dope condition poly aniline, or its derivative and matrix high molecular compound will not be limited especially if the conductivity after thin-film-izing is more than 10-9 (S/cm). Although there is no limitation special to the approach of mixing with the poly aniline constituent used for this invention and a matrix high molecular compound, it is desirable to mix in the state of distribution or a solution. For example, mixing distribution of a dope condition poly aniline, or a solution and the solution of a high molecular compound, or adding a solvent at once, and distributing or dissolving each etc. is not limited especially.

[0029] A conductive thin film is obtained by making a base material apply and dry the distribution or the solution containing the poly aniline used for this invention. As a base material which applies a dope condition poly aniline or its derivative, they are a resin fabrication article, plastic film, a synthetic paper, fiber, etc. A resin fabrication article means the thing of configurations other than these by this invention, although it is the fabrication article obtained by carrying out size enlargement using heat and/or a solvent and a film, a synthetic paper, and fiber are also contained in a wide sense using thermoplasticity and/or thermosetting resin. Moreover, what processes it further and is obtained is contained, using a primary fabrication article as a material. For example, especially if the material of a resin fabrication article does not invade the poly aniline to the solvent which distributes or dissolves, it is not limited, but polyester, polystyrene, polyethylene, a polyamide, a polyvinyl chloride, polyvinyl acetate, polypropylene, a styrene-butadiene copolymer, polybutadiene, a polysiloxane, a polycarbonate, a polyacrylonitrile, polymethylmethacrylate, ABS plastics, etc. are mentioned, and, specifically, there is no limitation also in a configuration. Polyester, polyethylene, polypropylene, a polyamide, a polycarbonate, etc. are raised as a material of plastic film. The thing of polyester and a polypropylene system is mentioned as a synthetic paper. As fiber, it is a natural fiber, a chemical fiber, a synthetic fiber, an inorganic fiber, etc., and they are specifically inorganic fibers, such as synthetic fibers, such as chemical fibers, such as natural fibers, such as cotton, wool, and silk, and rayon, polyester, and polyamide acrylic polyethylene polypropylene polyurethane, and glass, carbon, etc.

[0030] About the approach of making a thin film forming on a base material front face, there is especially no limitation, and it is easily possible by applying a base material by the approach of a dipping, brushing, a roller coat, a spray coat, etc., and making it dry with distribution, the solution, the mixed dispersion liquid of the poly aniline and a matrix macromolecule, or the solution of the poly aniline, and can apply also with the base material of a large area and a long picture. Especially the thickness of a thin film is not limited but is determined from the conductivity of the constituent of a surface-electrical-resistance value and the poly aniline for which it asks. When covering the poly aniline of the same conductivity, thickness and a surface-electrical-resistance value have the relation of an inverse proportion.

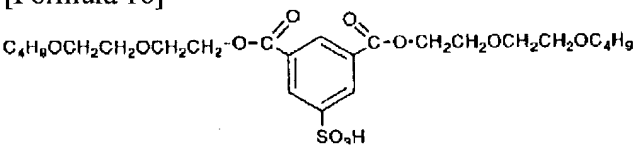
[0031] The conductive thin film obtained from the poly aniline used for this invention has the following

descriptions, and is very useful as antistatic film, such as a resin fabrication article, plastic film, a synthetic paper, and fiber. i) ii with few humidity dependencies iv which does not spoil the dynamic physical properties of base material original since it is a thin film excellent in transparency on an iii front face v with wash-proof nature especially high as an antistatic agent for fiber with a high water resisting property Conductivity is comparatively high and it is arbitration. Surface electrical resistance (103-1010ohm/**) is possible.
[0032]
[Effect of the Invention] The solution of the poly aniline which is distributing or dissolving in the state of a dope by this invention can be applied on a direct base material, and a solvent can be removed and thin-film-ized. Thus, the created thin film has high conductivity and stability. a resin fabrication article and plastic film -- concrete -- the film for transparence record (the object for transparence thermal recording --) The film for [, such as an object for transparence electrostatic recording] ceramic ** types, the film for chip carriers, A transparency sheet, the film for floppy disks, a micro X-ray film, A dry film and dry heat transparency sheet, the film for tray JINGU, It is used suitable for electrification prevention of a synthetic paper, nature, a composition, a semi-synthetic fiber, etc., etc. outside the film for a conductive package, the film for magnetic tapes, the films (a floor, a wall, head lining, etc.) for clean rooms, the other films for sensitive material, etc. Moreover, after mixing with other polymeric materials in dispersion liquid or a solution, thin-film-izing is also possible.
[0033]
[Example] Although an example is given to below and this invention is explained to it, this invention is not limited at all by these examples. The appraisal method used for this invention is shown below.
[0034] Surface electrical resistance: It measured under applied-voltage 500V and 25-degree C conditions with the specific resistance measuring instrument by Takeda Riken.
[0035] Electrification damping time: It was with the static decay meter made from U.S. ETS, the electrical potential difference of 5.0kV was impressed to inter-electrode on both sides of the sample in 23 degrees C and 15%RH ambient atmosphere, and the damping time t99 after grounding and grounding an electrode in the place where applied voltage became 5.0kV until applied voltage is set to 0.05kV was measured.
[0036] Adhesion: After mincing the base eye with the cutter knife on the surface of the thin film and sticking a cellophane tape, it exfoliated and the number which remained among 100 grids was counted.
[0037] Pencil degree of hardness: To JIS-K-5401 law, therefore, the pencil length **** test coupon was used and it examined by the existence of a 200g [of loads] blemish.
[0038] Water resisting property: The dipping of the base material which made the thin film cover was carried out underwater, and the surface electrical resistance in front of the dipping when leaving it at a room temperature was compared.
[0039]
[The synthetic example 1] After the solution which dissolved 24.5g of ammonium persulfates in 70g of distilled water was dropped in 1 hour, having added aniline 15g, 270g of distilled water, and 36g of concentrated hydrochloric acid, and maintaining at the temperature of 0 degree C, it agitated for further 4 hours. After carrying out the ** exception and performing rinsing, a methanol, and ether washing, the vacuum drying was carried out and poly aniline 12.4g was obtained. After adding 10g of the obtained poly aniline to 1000g of aqueous ammonia 3% and agitating at a room temperature for 2 hours, it carried out the ** exception and rinsing, methanol swabbing, and ether washing were performed. The vacuum drying was carried out and the 6.5g dedope poly aniline (EMERARU gin base) was obtained. When it was made to dissolve in N-methyl pyrrolidone and GPC was measured, number average molecular weight 27000 and weight average molecular weight were 99000 in polystyrene conversion.
[0040]
[The synthetic example 2] As 5-sulfo sodium isophthalic acid dimethyl 27.8g, diethylene-glycol-Monod n-butyl ether 207.8g, and an esterification catalyst, 0.067g of zinc acetate was added to 300ml 3 opening flask equipped with a stirrer, distilling-off object draw tubing, and a thermometer, and it reacted to it at 210 degrees C for 8 hours. It took to reaction advance, and became a transparence homogeneity liquid from white suspension, and the methanol of computational complexity distilled. Unreacted diethylene-glycol-Monod n-butyl ether was distilled by 220 more degrees C and 70mmHg in 2 hours.
[0041]
[The synthetic example 3] 20g (the ORGANO CORP. make, arbor list 15) of ion-exchange resin was added to 30ml of THF solutions of 1g of diester compounds obtained in the synthetic example 2, and it agitated for 15 minutes at the room temperature. The glass filter washed ion exchange resin by THF30ml again the back

according to **, and it united with filtrate. It confirmed titrating in the sodium-hydroxide water solution of 0.02 conventions, and being quantitatively changed into the sulfonic acid by the sulfo sodium group. THF is distilled off and a residue is dried -- the structure of a formula (9) was checked by 1 H-NMR and IR.

[0042]

[Formula 16]



式（9）

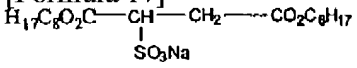
When ultrasonic irradiation of dedope poly aniline 0.10g and the 0.30g (molecular weight 534) of the above-mentioned sulfonic acid type diester compounds obtained in the synthetic example 1 was added and carried out to THF8ml, the solution of uniform dark green was obtained in 3 hours. When this solution was filtered with the glass filter, the insoluble matter which remained on the filter was very little. Applied this dope condition poly aniline THF solution on the polyethylene terephthalate film, it was made to dry at 120 degrees C for 1 hour, and the thin film of 1 micrometer of thickness was obtained. When measured by the one terminal pair network. method about the obtained thin film, it was conductivity sigma=12 (S/cm). The dope condition poly aniline was dissolved in 2-n-butoxy ethanol by the same approach, and the thin film was made to form. It was conductivity sigma=9 (S/cm).

[0043]

[The synthetic example 4] Ion exchange treatment of the compound of formula (10) - (14) was carried out similarly, after the structure check, ultrasonic irradiation was carried out to the dedope poly aniline of the equivalent in THF, and the uniform dark green solution was obtained. After filtering, applied the dope condition poly aniline THF solution on the polyethylene terephthalate film, it was made to dry at 120 degrees C for 1 hour, and the thin film of 1 micrometer of thickness was obtained. Conductivity was measured by the one terminal pair network method about the obtained thin film. A result is shown in Table 1.

[0044]

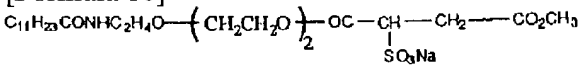
[Formula 17]



式（10）

[0045]

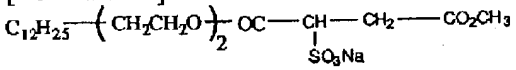
[Formula 18]



式（11）

[0046]

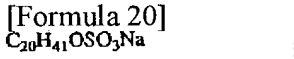
[Formula 19]



式（12）

[0047]

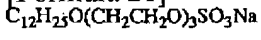
[Formula 20]



式（13）

[0048]

[Formula 21]



式（14）

[0049]

[Table 1]

ドーパント	(ドーパント分子量) ／N	導電率σ (S／cm)
式 (10)	422	1.2×10^{-2}
式 (11)	525	6.7×10^{-2}
式 (12)	452	3.6×10^{-2}
式 (13)	378	1.7×10^{-2}
式 (14)	398	2.9×10^{-2}

[0050]
[The synthetic example 5] When ultrasonic irradiation of the 0.23g of the sulfonic acid type compounds of dedope poly aniline 0.10g and the formula (10) origin obtained in the synthetic example 1 was added and carried out to 2-n-butoxy ethanol 15ml, the solution of uniform dark green was obtained in 3 hours. When this solution was filtered with the glass filter, the insoluble matter which remained on the filter was very little.
[0051]
[The synthetic example 6] When ultrasonic irradiation of the 0.23g of the sulfonic acid type compounds of dedope poly aniline 0.10g and the formula (10) origin obtained in the synthetic example 1 was added and carried out to toluene 15ml, the solution of uniform dark green was obtained in 3 hours. When this solution was filtered with the glass filter, the insoluble matter which remained on the filter was very little.
[0052]
[The synthetic example 7] 2, 2'-dinaphthyl methane -6, and 2.5g of 6'-disulfon acid sodium salt were melted into 10ml of distilled water, and methanol 70ml mixed liquor, 37.5g (Amberlyst 15) of ion-exchange resin was added, and it agitated for 15 minutes at the room temperature. It titrated in the sodium-hydroxide water solution of 0.02 conventions the back according to ** with the glass filter, and confirmed that the sulfo sodium group was quantitatively changed into the sulfonic group. a solvent is distilled off and residue is dried -- structure was checked by 1 H-NMR and IR. 2 obtained and 2'-dinaphthyl methane - 6 and 6 -- '- disulfon acids 2.4g and 2 and 2' - dinaphthyl methane -6 and 6' -- added 2.7g of - disulfon acid sodium salt to 10ml of distilled water, melted it, agitated at the room temperature for 30 minutes, the ionic equilibrium was made to reach, and it considered as the dopant solution.
[0053]
[The synthetic example 8] 13ml of dopant (molecular weight 450) solutions of the synthetic example 7 and aniline 0.5g were put in, it cooled at 0 degree C, and the ferrous sulfate of a minute amount was added. It cools at 0 degree C beforehand, and the solution which dissolved 1.2g of ammonium persulfates in 4ml of water was dropped in 10 minutes. The reaction mixture was kept at 0 degree C, and was agitated for 20 hours. It was dissolving in water and the generated dope poly aniline was dialyzed for two days (the product made from Spectrum Medical Industries, the spectra/pore 7, FE-0521-05). When carried out the vacuum drying of some solutions, solid content concentration was determined, and the poly aniline obtained further was pressed into the pellet and having been measured with the four probe method, it was conductivity sigma=2.2x10-3 (S/cm). This poly aniline 0.1g was processed at the room temperature by 10ml of aqueous ammonia 3% for 2 hours, the ** exception, it rinsed and dried and the dedope poly aniline was obtained. When the dedope poly aniline was dissolved in NMP and GPC was performed, in polystyrene conversion, number average molecular weight was 12000 and weight average molecular weight was 23000.
[0054]
[The example 1 of a comparison] Although ultrasonic irradiation of the dedope poly aniline 0.1g obtained in 0.18g (molecular weight 326) of dodecylbenzenesulfonic acid and the example 1 of reference was added and carried out to toluene 10ml for 3 hours, it hardly dissolved but the poly aniline precipitated. It was the same result even if it changed the solution into THF, chloroform, or 2-n-butoxy ethanol.
[0055]
[Example 1] the THF solution of the dope poly aniline obtained in the synthetic example 3, and the Toyobo make -- the THF solution of Byron resin RV-280 was mixed at a various rate, it was made to apply and thin-film-ize on a polyethylene terephthalate film (1 micrometer of thickness), and conductivity was measured. A result is shown in drawing 1 . the flume gap which observes a thin film with an optical microscope (400 times) -- comparatively -- in -- phase separation was not seen. When the percentages of a dope poly aniline were 15, 20, 30, and 50wt%, the adhesion of a thin film was 100% and the pencil degree of hardness was 2H.

[0056]
[Example 2] The water solution of a dope poly aniline and the water dispersion of Toyobo Byron resin MD 1200 which were obtained in the synthetic example 8 were mixed at a various rate, it was made to apply and thin-film-ize on a polyethylene terephthalate film (1 micrometer of thickness), and conductivity was measured. A result is shown in drawing 1 . the flume gap which observes a thin film with an optical microscope (400 times) -- comparatively -- in -- phase separation was not seen. When the percentages of a dope poly aniline were 10, 20, 30, and 50wt%, the adhesion of a thin film was 100% and the pencil degree of hardness was 2H.
[0057]
[Example 3] the THF solution of the dope poly aniline obtained in the synthetic example 3, and the Toyobo make -- the THF solution of Byron resin RV-280 was mixed so that the rate of a dope poly aniline might become 20wt(s)%, and the solution of 1% concentration of solid content was prepared. It was made to apply and thin-film-ize by the bar coating machine on a polyethylene terephthalate film. With the transmission electron microscope, thickness was measured with 0.01 micrometers. It was surface-electrical-resistance Rs =1.3x109 (omega/**), and the electrification damping time was 0.48 seconds. Similarly, from this solution, surface electrical resistance is changed, a thin film is created, and the result of having measured each permeability (550mm) is shown in drawing 2 .
[0058]
[Example 4] the THF solution of the dope poly aniline similarly doped by the dopant of the formula (10) - (14) origin, and the Toyobo make -- the THF solution of Byron resin RV-280 was mixed so that the rate of a dope poly aniline might become 40wt(s)%, and the solution of 1% concentration of solid content was made to prepare and thin-film-ize Moreover, the water solution of a dope poly aniline and the water dispersion of Toyobo Byron resin MD 1200 which were obtained in the synthetic example 8 are mixed so that the weight ratio of a dope poly aniline may become 30%, and the solution of concentration was prepared 1% and it was made to thin-film-ize. A result is shown in Table 2.
[0059]
[Table 2]

ドーパント	膜厚（μm）	表面抵抗（Ω／□）	帯電減衰時間（s）
式（10）	0．2	1．7×10⁹	0．7
式（11）	0．3	3．1×10⁸	0．8
式（12）	0．2	5．2×10⁹	0．9
式（13）	0．4	2．8×10⁹	0．8
式（14）	0．2	6．1×10⁹	0．9
合成例（8）	0．1	1．5×10⁹	0．6

[0060]
[Example 5] the dope poly aniline obtained in the synthetic example 3, and the Toyobo make -- the mixed THF solution of Byron resin RV-280 was applied by the bar coating machine on the polyethylene terephthalate film, and the thin film of surface-electrical-resistance RS =1.1x1010, 2.0x108, and 7.2x104 (omega/**) was created. After putting each polyethylene terephthalate film which carried out the thin film coat for 24 hours on the bottom of relative humidity 15 and 50 or 65% ambient atmosphere, the result of having measured surface electrical resistance under the conditions is shown in drawing 3 . The result at the time of carrying out the coat of the conventional ionicity antistatic agent (Mitsuhiro formation make SANSUTATTO2012A) on a polyethylene terephthalate film as an example of reference is shown in this drawing by the dotted line. Time amount change of the surface electrical resistance of the surface electrical resistance after carrying out dipping processing of the polyethylene terephthalate film in which above surface-electrical-resistance RS =7.2x104 (omega/**) carried out the thin film coat at distilled water is shown in drawing 4 . Furthermore, although above surface-electrical-resistance RS =1.1x1010, 2.0x108, and the polyethylene terephthalate film that carried out the coat of the thin film of 7.2x104 (omega/**) were left for 1 minute at 230 degrees C among air, surface electrical resistance was changeless also in which sample.
[0061]
[Example 6] the dope poly aniline obtained in the synthetic example 3, and the Toyobo make -- the mixed THF

solution (poly aniline 20wt% and solid content 1wt%) of Byron resin RV-280 was applied by the bar coating machine on the polypropylene plate (100mmx100mmx5mm), and the thin film of surface-electrical-resistance RS =8.1x108 (omega/**) was created. The electrification damping time was 0.54 seconds. Although surface electrical resistance was measured after putting the synthetic paper which carried out the thin film coat for 24 hours on the bottom of relative humidity 15 and 50 or 65% ambient atmosphere, it was the same value under which condition. Although the dipping was furthermore carried out to distilled water at the room temperature for 24 hours, change was not accepted in surface electrical resistance.

[0062]

[Example 7] the dope poly aniline obtained in the synthetic example 3, and the Toyobo make -- the mixed THF solution (poly aniline 20wt% and solid content 1wt%) of Byron resin RV-280 was applied by the bar coating machine on Toyobo polyester system synthetic paper Chris Per, and the thin film of surface-electrical-resistance RS =4.3x108 (omega/**) was created. The electrification damping time was 0.41 seconds. Although surface electrical resistance was measured after putting the synthetic paper which carried out the thin film coat for 24 hours on the bottom of relative humidity 15 and 50 or 65% ambient atmosphere, it was the same value under which condition. Furthermore, it is i. They are a dipping and ii at a 24-hour room temperature to distilled water. Although it was left for 1 minute at 230 degrees C among air, in any case, surface electrical resistance is before and after processing, and it was changeless.

[0063]

[Example 8] the dope poly aniline of the synthetic example 3, and the Toyobo make -- the dipping of cotton yarn, wool yarn, polyester yarn, and the nylon yarn was carried out to the THF solution (poly aniline 20wt%, 1% of solid content) of Byron resin RV-280, and it dried for 10 minutes at 120 degrees C. After repeating this actuation 3 times, the electrification damping time was measured about each fiber, and it compared with the unsettled thing (Table 3). Furthermore, the electrification damping time after carrying out the dipping of each fiber to distilled water at a room temperature for 24 hours is also shown.

[0064]

[Table 3]

	綿	羊毛	ポリエステル	ナイロン
帯電減衰時間（s）	0．18	0．14	0．35	0．22
水浸せき後（s）	0．22	0．19	0．42	0．29
未処理（s）	180	162	231	207

It was checked from the observation using an electron microscope that the thin film of the poly aniline has covered the fiber front face to homogeneity.

[Translation done.]